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REPORT OF INVESTIGATIONS/1994

Environmental Impacts of Mine Waste Sandfill

By R. L. Levens and C. M. K. Boldt

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

U.S. Department of the Interior
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Bruce Babbitt, Secretary

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International Standard Serial Number
ISSN 1066-5552

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm^3	cubic centimeter	m/s	meter per second
g/mt	gram per metric ton	mt	metric ton
m	meter	pct	percent
mL	milliliter	S	siemen
μm	micrometer	V	volt
mmol	millimole		

ENVIRONMENTAL IMPACTS OF MINE WASTE SANDFILL

By R. L. Levens[1] and C. M. K. Boldt[2]

ABSTRACT

The Underground Injection Control program was promulgated in 1981 by the U.S. Environmental Protection Agency under the provisions of the Safe Drinking Water Act. Placement of mine waste backfill underground is considered underground injection under the provisions of this program. A major issue is whether mine waste that is regulated as a contaminant source on the surface should be disposed of underground.

The U.S. Bureau of Mines conducted research to investigate the impacts of mine waste sandfill on the quality of ground water. Analyses of water samples collected before and after contact with sandfill in a 10-year-old stope, as well as samples of the sandfill itself, were used to ascertain the influence of the sandfill after mine closure and subsequent flooding. Computer models supported the hypothesis that oxidation of pyrite by oxygen, accompanied by dissolution of carbonates, was the predominant reaction controlling the quality of the water being discharged from the stope. Concentrations of metals released as a result of acid production remained near or below detection limits. Metals release after mine flooding is expected to remain low as a result of the buffering by the sandfill and the reduced rate of oxidation.

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INTRODUCTION

BACKGROUND

The Safe Drinking Water Act (P.L. 95-190) was enacted in 1974 by the U.S. Congress to develop regulations to protect the Nation's underground sources of drinking water. One resultant regulatory program, the Underground Injection Control (UIC) program, was promulgated in 1981 by the U.S. Environmental Protection Agency (EPA). Within the UIC program, a Class V well includes "sand backfill and other backfill wells used to inject a mixture of water and sand, mill tailings, or other solids into mined-out portions of subsurface mines whether what is injected is a radioactive waste or not" [40 CFR 146.5(e)(8) (*25*)].[3] A well is broadly defined as either a dug hole or a bored, drilled, or driven shaft whose depth is greater than its largest surface dimension.

Because placement of mine waste backfill in underground openings is considered to be underground injection under UIC regulations, the impact on mine backfilling practices could be extensive. Currently, over 20 metal mines in the United States use backfill materials ranging from quarried rock to cemented mill tailings. The major purpose of the backfill is to support the ground during mining; however, backfilling is increasingly considered as a means to minimize surface disposal of mine waste.

Water affected by backfilling during active mining is usually pumped to the surface where its disposal is regulated as surface discharge. Backfilled areas may become flooded after a mine is closed, possibly resulting in contamination of ground water. Therefore, in contrast to regulations addressing surface disposal, regulations concerning the contamination of ground water after mine closure will be a primary focus under the UIC program.

Returning mine waste to the original excavation is an attractive option because the original minerals are stable in that environment. However, chemical transformations that occur during the milling process, as well as after placement underground, may produce less stable minerals. Also, the hydraulic conductivity of uncemented sandfill will probably be several orders of magnitude greater than the surrounding rock because of the mechanical destruction of the original rock during milling. Uncemented sandfill with higher hydraulic conductivity than the surrounding rock may provide preferential pathways for ground water flow, which may in turn enhance leaching of metals from the backfill.

The mechanisms controlling dissolution of minerals in sandfill and the mobility of heavy metals change when sandfill becomes flooded after mine closure. The nature of these changes must be considered to estimate the impacts of mine waste backfill on ground water. For example, reduced amounts of oxygen (O_2) are expected to limit the oxidation of sulfides as well as the precipitation of hydroxides.

PURPOSE AND OBJECTIVES

The purpose of this research by the U.S. Bureau of Mines (USBM) was to study the possible impacts of mine waste sandfill on the quality of ground water in the rock surrounding a stope. The objectives were to document the impacts of sandfill on water discharging from a selected sandfilled stope, to investigate possible geochemical controls on the mobility of metals retained in the sandfill, and to discuss the factors expected to determine the long-term impacts of sandfill after mine closure and subsequent mine flooding.

HYDROCHEMISTRY

Oxidation of sulfides, such as pyrite (FeS_2), and associated dissolution of other minerals control the chemical composition of water draining from sulfide mines. Initially, pyrite is oxidized by O_2 in the presence of water, yielding sulfate ion (SO_4^{2-}), ferrous ion (Fe^{2+}), and hydrogen ion (H^+). Next, Fe^{2+} is oxidized by O_2 to ferric ion (Fe^{3+}). This second step is catalyzed by the bacteria *Thiobacillus ferrooxidans*. Pyrite is oxidized by Fe^{3+}, yielding additional Fe^{2+}, SO_4^{2-}, and H^+ in the final step [Lowson, 1982 (*17*)].[3] The three steps of the oxidation of pyrite are given below.

$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+. \quad (A)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O. \quad (B)$$

$$FeS_2(s) + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+. \quad (C)$$

Ferrous ion, sulfate ion, and hydrogen ion are released into solution through pyrite oxidation. Ferric ion may

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

precipitate as ferrihydrite [$Fe(OH)_3$], goethite [FeO(OH)], or jarosite [$KFe_3(SO_4)_2(OH)_6$], collectively known as "yellow boy." The solubility of Fe^{3+} increases at low pH values (<4.5) and is reduced during oxidation of additional pyrite. Ferric ion becomes the dominant oxidizing agent below pH 3.0. The presence of *T. ferroxidans* greatly increases the rate at which Fe^{2+} is oxidized, thereby perpetuating the oxidation of pyrite by Fe^{3+}.

The H^+ produced during oxidation of pyrite may be consumed in reactions involving carbonate and silicate minerals, releasing major ions, including calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), bicarbonate (HCO_3^-), and silisic acid (H_4SiO_4). Typical reactions involving calcite ($CaCO_3$) and olivine (Mg_2SiO_4) are given below.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-. \qquad (D)$$

$$Mg_2SiO_4 + 4\,H^+ \rightarrow 2\,Mg^{2+} + H_4SiO_4. \qquad (E)$$

Metals other than iron (Fe) also may be leached from the ore, backfill, or country rock by acidic water. The resulting concentrations of heavy metals are controlled by the buffering capacity of the geochemical system and oxidation-reduction reactions, dissolution-precipitation reactions, or desorption-adsorption reactions. The buffering capacity of the system is determined to a great extent by the geochemistry of the major ions. Therefore, knowledge of the dissolution and precipitation reactions involving the major ions is a key to understanding the mobility of metals.

RELATED RESEARCH

Previous studies in which the effects of backfill materials on ground water were investigated have been primarily limited to coal and uranium tailings. The contamination potential of coal waste backfill in surface and underground mines has been studied by Geidel and Caruccio [1982 (*9*)], Henderson and Norton [1984 (*11*)], McCurry and Rauch [1986 (*18*)], Senyur [1989 (*21*)], and Snow [1990 (*22*)]. The important considerations in these studies were the potential for acid production and the amount of waterflow through the wastes. Snow [1990 (*22*)] concluded that flooding mine workings to control acid mine drainage is difficult when the workings are located above the drainage level. Sealing mines with fly ash was proposed by Snow [1990 (*22*)] to facilitate flooding under these circumstances. Senyur [1989 (*21*)] observed decreases in the permeability of backfill and the rate of waterflow through the backfill over time.

The applicability of using coal mine case studies in an investigation of the environmental impacts of backfill in metal mines is limited, however. The primary difference between the two types of mines is the release of heavy metals as a result of oxidation of sulfides in metal mines.

Studies of the impacts of uranium mill tailings backfill have been extensive [Brookins, Thomson, and Longmire, 1982 (*2*); Longmire, Hicks, and Brookins, 1981 (*16*); Thomson and Heggen, 1982 (*23*); Thomson, Longmire, and Brookins, 1986 (*24*)]. Field samples of tailings, backfill, and water drainage from backfill were used to interpret geochemical transformations in the backfill. The fate of heavy metals contained in the uranium tailings was considered, as well as the fate of the radioactive constituents. The authors concluded that the short- and long-term environmental impacts of backfill associated with active mining and postclosure activities were negligible.

Factors controlling metal release from surface tailings impoundments have been investigated through the use of leaching columns and simulated rain water [Doepker, 1991 (*3*); Doepker and O'Conner, 1990 (*6-7*)]. The factors investigated included degree of saturation; availability of O_2; wet-dry cycles; leachate residence time; buffering capacity of tailings; evaporation of pore waters; composition of host rock; composition, amount, and rate of formation of secondary minerals; and leachant pH, ionic strength, and types of ions present. The major cause of metal dissolution was found to be oxidation of sulfide minerals by O_2 under partially saturated conditions. Enhanced metal dissolution was observed following alternating wet and dry periods or after extended drying periods. Furthermore, reduced partial pressure of O_2 was determined to be the only way to minimize metals release from sulfidic tailings. Concentrations in leachates from well-oxidized tailings differed from concentrations from fresh tailings because secondary minerals may be more or less soluble than primary minerals. Secondary minerals may be formed in sandfill under partially saturated conditions before a mine is flooded; a temporary increase in metal mobility may occur as these minerals become more soluble after flooding.

The effects of several factors on metal dissolution from submerged tailings were investigated using batch tests [Doepker and Drake, 1991 (*4*)]. Oxidation of sulfide minerals in submerged tailings was much slower than oxidation in nonsubmerged tailings because O_2 diffuses slowly in water. Metals were released from submerged oxidized tailings even when they were neutralized because of the dissolution of secondary minerals. Thus, a short-term release of metals from secondary minerals may occur as a backfilled stope becomes submerged. However, metals

release would be expected to decrease as secondary minerals were depleted from the tailings.

The primary issues identified in earlier research were flooding of placed backfill, allowing tailings to dry, mechanically dewatering sandfill prior to backfilling, the buffering capacities of backfill, and the extent of backfill oxidation [Brookins, Thomson, and Longmire, 1982 (*2*); Doepker and Drake, 1991 (*5*); Thomson, Longmire, and Brookins, 1986 (*24*)].

METHODOLOGY

This research is part of a larger effort in which the impacts of mine waste backfill on water quality are being investigated at four underground sulfide mines [Levens and Boldt, 1992 (*15*)]. Backfill materials used in the four mines included cemented total gradation tailings; uncemented, classified sand; and uncemented, low-grade gob.

Water samples were gathered monthly from seeps above and directly below a sandfilled stope in an underground mine in northern Idaho. Cation and anion concentrations in samples were compared to determine if meaningful differences could be detected and attributed to the backfill material, in this case, sandfill. Mineral assays of sandfill from the test stope, published mineralogic descriptions, and information from mine records were used to determine the minerals that might have been sources of the major ions in solution. Samples of the sandfill were also leached with acid to determine the degree to which metals were available for dissolution.

Two geochemical computer models, WATEQ4F [Ball, Nordstrom, and Zachmann, 1987 (*1*)] and BALANCE [Parkhurst, Plummer, and Thorstenson, 1982 (*19*)], were used to investigate the geochemical reactions involving the major ions. WATEQ4F is a thermodynamically based model that computes element speciation and mineral saturation in water samples. Saturation indices provide a basis for evaluating the potential for dissolution and precipitation reactions between minerals in backfill and infiltrating water. Knowledge of reaction kinetics and mineral stability ranges are necessary for interpreting the validity of the thermodynamic approach used by WATEQ4F.

BALANCE is used in conjunction with WATEQ4F to define and quantify the mass transfer between infiltrating water and backfill materials. The primary use of WATEQ4F and BALANCE is to investigate whether dissolution of carbonate minerals is buffering acid produced from sulfide oxidation. Again, kinetic controls on mineral dissolution are not addressed in WATEQ4F or BALANCE.

Laboratory research on mechanisms controlling mineral dissolution, as well as investigations of the subaqueous disposal of tailings, provides a basis on which to predict the long-term hydrochemical impacts of sandfill after mine flooding. Important factors to be considered include the mechanisms that control mineral solubilities in sandfill, the effect of oxidation of sandfill prior to flooding, and the potential for migration of heavy metals from flooded sandfill.

The testsite, located in the Coeur d'Alene Mining District of northern Idaho, is a moderately deep underground lead-zinc mine. The geologic formations encountered in the mine consist of Precambrian metasediments, including quartzites, argillites, siltites, and minor amounts of carbonates. Galena (PbS) and sphalerite (ZnS) are the principal ore minerals, while quartz, siderite ($FeCO_3$), and pyrite are the principal gangue minerals. Quartz, sericite or illite, and iron-rich carbonates [primarily ankerite ($CaFe(CO_3)_2$)] are the principal minerals found in the wall rock. Ore was mined by conventional cut-and-fill methods, and backfill consisted of tailings classified using cyclones (sandfill).

A complex pattern of faults and folds characterizes the geologic structure surrounding the testsite. The mine was developed along a series of subparallel shear faults that coincide with the axial trace of an overturned anticline [Juras, 1982 (*13*)]. Lesser faults and fractures divide the blocks located between the shear faults [Haskell, 1987 (*10*)].

Ground water recharge to the bedrock in the vicinity of the mine results from infiltration from overlying surface drainage basins [Hunt, 1983 (*12*)]. The drainage basins are underlain by variably fractured bedrock except in areas where narrow strips of alluvium are found along stream channels. Peak stream discharge occurs when snow melts in late winter and early spring. Streamflow diminishes from early summer until late fall. Ground water inflow to mine openings follows the same temporal pattern as does streamflow.

The unfractured rock surrounding the mine is of very low hydraulic conductivity; consequently, water infiltrates the bedrock along the fractures and faults. Similarly, water from the bedrock enters the mine where fractures and faults are intersected by backfilled or open mine workings. The hydraulic conductivity of the fractured bedrock was estimated at 1×10^{-7} m/s by Lachmar [1988 (*14*)]. For comparison, the hydraulic conductivity of the very fine grained sandfill used in the mine was calculated from its grain-size distribution to be 1×10^{-5} m/s using the Hazen equation [Freeze and Cherry, 1979 (*8*)].

Acid mine drainage containing high concentrations of dissolved solids is produced within parts of the mine through oxidation of pyrite and subsequent dissolution of

other minerals. Table 1 shows concentrations of dissolved constituents detected in water as it enters the mine and in water from an acid-producing area of the mine [Riley, 1990 (*20*)]. Water from the acid-producing areas of the mine is characterized by high concentrations of SO_4^{2-}, Fe, Ca (calcium), Mg (magnesium), Mn (manganese), Al (aluminum), and heavy metals, as well as by low pH. The primary controls on acid production are the mineralogy of the rock and the availability of O_2 and water [Riley, 1990 (*20*)]. Water quality within the mine is highly variable because acid production from pyrite oxidation is significant only in isolated areas.

Table 1.—Range of concentrations of dissolved elements in test mine, milligrams per liter

Constituent	Recharge	Acid mine drainage
Element:		
Al	<0.01	412.00
Ca	9.70	574.00
Cl	0.08	0.28
Fe	<0.01	17,900.00
Mg	0.43	2,230.00
Mn	<0.01	3,030.00
Na	0.24	0.01
S	0.25	28,300.00
Si	3.59	63.30
Zn	0.02	10,000.00
HCO_3	0.53	0.01
pH	7.40	2.20
EC S	0.07	55.20

EC Electrical conductance.

The stope selected for this study is the 17-level stope on the Barr vein, which is also known as the Barr stope (stope 170-21-23 in mine records). The Barr stope consists of three intervals separated by horizontal pillars that were mined between 1973 and 1981 (fig. 1). Other sandfilled stopes overlie the Barr stope. Rocks in the vicinity of the Barr stope consist of sericitic or vitreous quartzites interbedded with infrequent argillite layers. Approximately 21,700 mt of ore was extracted from a discontinuous, fault-controlled, sulfide ore body. Average ore grade was 5.46 pct Pb (lead), 77.5 g/mt Ag (silver), and 0.72 pct Zn (zinc). The Barr stope is not located in the most serious acid-producing part of the mine [Riley, 1990 (*20*)].

Water enters mine openings near the Barr stope along a series of minor faults. Ground water is believed to recharge the stope through these minor faults as well as through drainage from overlying sandfilled stopes. The relative contribution from mine inflow versus drainage from overlying stopes was not determined. Water from the Barr stope drains into collection sumps and is pumped to the surface for discharge. Precipitates of ferrihydrite and carbonates or gypsum ($CaSO_4 \cdot 2H_2O$) are abundant in the drift below the Barr stope and in the manway through the stope.

Samples of backfill were collected from the Barr stope and from the underground secondary cyclone discharge circuit at the mine. All samples were sent to the USBM's Reno Research Center for chemical assay and mineral identification by X-ray diffraction (XRD). The chemical assay method used was lithium borate fusion followed by acid digestion using hydrochloric acid (HCl) and inductively coupled plasma (ICP) analysis. A maximum leachability assay of samples of each backfill material also

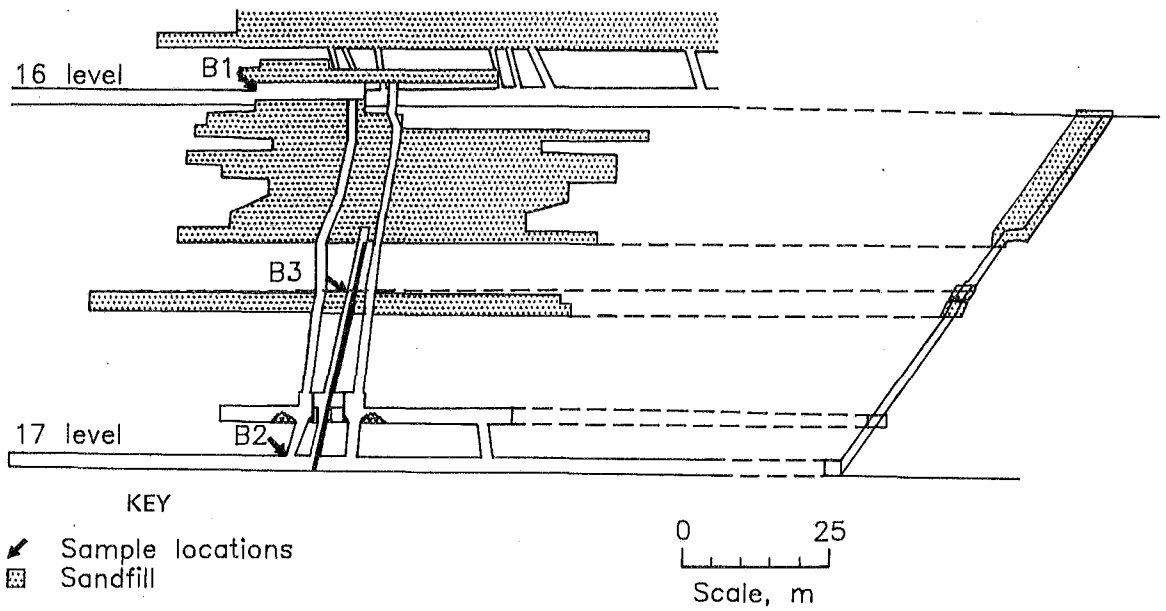

Figure 1.—Two-dimensional schematic of Barr stope workings and field sampling sites.

was conducted using a mixture of HCl (22 cm^3), HNO_3 (nitric acid) (4 cm^3), and H_2O (20 cm^3) at the USBM's Spokane Research Center (SRC) to determine the maximum leachable quantities of metals. The maximum leachability assay was not intended to replicate natural conditions, but to show the presence of metals that could be released under highly acidic conditions.

Water samples were collected both before and after the water came into contact with the sandfill to determine the impacts of placed mine waste backfill on water quality. Sampling was initiated in November 1990 and continued on a monthly basis through May 1991. The sampling program was constrained by the difficulty of access to the backfilled stopes, by the presence of water seeps, and by the cost of obtaining and analyzing additional samples.

One monitoring site (B1) was located near the top of the Barr stope and two others (B2 and B3) near the bottom. The upper and lower levels are approximately 425 and 490 m, respectively, below the main haulage level in an inactive portion of the mine.

Mining in the study area progressed in stages. Two cuts separated by horizontal pillars lie below the main stope but above the lower access level. Water recharging the stope was collected at B1. A water sample was not obtained from below the stope during the first month, but samples collected during the second and third months were taken from an ore chute beneath the cuts (B2). Samples from B2 represent a mix of water from several seeps from the sandfill along the ore chute.

Water samples collected after the third month were obtained from a tarp stretched across a manway immediately beneath the main portion of the stope and above the bottom two cuts (B3). A hose was strung between the tarp and the lower access level. Samples were collected from both B2 and B3 during month 7 for comparison. No samples were obtained during month 4, and sampling was suspended after month 7 when the mine hoists were shut down.

The pH, specific electrical conductance (EC), redox potential (Eh), temperature, and alkalinity of samples were measured in the field. Samples were vacuum filtered through 0.45-μm filters and placed in 50-mL polyethylene bottles. Separate bottles were filled for cation analysis using the Perkin-Elmer Plasma II[4] ICP spectrometer and for anion analysis using a Dionex Series 4000i gradient ion chromatograph. Samples for cation analysis were preserved with HNO_3 according to EPA procedures [1983 (*26*)] to stabilize ions in solution. Samples were then transported to the chemistry laboratory at SRC and stored in a refrigerator until tested.

DATA PRESENTATION AND ANALYSIS

CHEMICAL ASSAY

Chemical assays show that approximately one-third of both the backfill from the Barr stope (old sandfill) and the backfill from the secondary cyclone discharge circuit (new sandfill) consists of silicon (Si) (table 2). Significant quantities of Al, Ca, Mg, K (potassium), Mn, and Fe, as well as measurable quantities of As (arsenic), Ba (barium), Na (sodium), Cd (cadmium), Co (cobalt), Cr (chromium), Cu (copper), Ni (nickel), Pb, and Zn were also detected in samples from both backfills. Analysis by XRD indicated both sandfill samples consist of quartz with traces of muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$], pyrite, and siderite.

The most notable differences between assays of the old and new sandfill samples were higher concentrations of As, Cu, and Zn, and lower concentrations of Mn in the new sandfill. These differences can be explained either by differences in metallurgical methods, differences in ore mineralogy, or by leaching of As, Cu, and Zn from the old sandfill.

MAXIMUM LEACHABILITY ASSAY

Calcium, magnesium, and sulfur (S) were the most prominent major ions leached from the backfill samples using a mixture of HCl and HNO_3 (table 3). Significant quantities of Pb, Zn, Mn, Fe, and As and lesser quantities of Cd, Co, Cr, Ni, and Al were also leached from the backfill samples.

The most notable differences between leachates from the new and old sandfill samples were higher concentrations of As, S, and Zn, and lower concentrations of Fe and Mn leached from the new sandfill. The higher SO_4^{2-} concentrations in leachate from the new sandfill may be the result of previous removal of SO_4^{2-} from the old sandfill as a result of sulfide oxidation and subsequent leaching of SO_4^{2-}. The higher Fe and Mn concentrations in leachate from the old sandfill may have been derived from the

[4]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

more-soluble, oxidized secondary minerals in the old sandfill. Arsenic and zinc may have already been leached from the old sandfill, explaining why concentrations of these elements were lower. However, because concentrations of other metals, including Cd, Co, Cr, and Cu, were not lower, or were only slightly lower, in the old sandfill, it is possible that differences in ore grade or metallurgical methods caused the differences in metal concentrations leached from the old sandfill.

Table 2.—Chemical assay of backfill materials, concentrations in parts per million

Element	Old sandfill	New sandfill
Al	15,000	14,000
As	[1]500	1,500
Ba	80	44
Ca	3,300	3,700
Cd	[1]8	13
Co	[1]20	30
Cr	[1]80	[1]100
Cu	250	620
Fe	57,000	54,000
K	5,800	5,100
Mg	2,400	1,400
Mn	5,000	1,600
Mo	<50	<50
Na	[1]600	[1]500
Ni	330	240
P	<1,000	<1,000
Pb	1,500	1,500
Si	348,000	358,000
Zn	2,500	5,800

[1]Near detection limit.

Table 3.—Maximum leachability of backfill materials, milligrams per liter

Element	Old sandfill	New sandfill
Ag	0.02	0.03
Al	1.97	1.87
As	5.95	10.45
B	.84	.51
Ba	.03	.02
Ca	35.40	38.80
Cd	.21	.34
Co	.13	.17
Cr	.40	.25
Cu	.56	.69
Fe	311.50	186.25
K	.90	.75
Mg	12.37	6.45
Mn	29.45	9.52
Na	.12	.41
Ni	.16	.21
P	.49	.39
Pb	21.55	27.79
S	37.65	85.75
Si	2.22	1.68
Zn	14.91	35.45

WATER QUALITY

Concentrations of dissolved constituents detected in water from the sampling sites were significantly lower than concentrations detected in the worst acid-producing portions of the mine (table 1). However, during one or more visits, concentrations of many constituents in water at the sampling sites exceeded concentrations in the mine recharge water, as well as maximum concentration levels (MCL's) allowed under the Safe Drinking Water Act. Of these constituents, only SO_4^{2-} consistently exceeded the MCL's (table 4).

The EC was higher at sites B2 and B3 than at B1. Increased concentrations of Ca, Mg, SO_4^{2-}, and HCO_3^- accounted for most of the increase. No meaningful changes in pH or concentrations of heavy metals were detected. The only meaningful differences between water quality at sites B2 and B3 on the 17 level were lower levels of HCO_3^- and Mn and higher levels of Fe at B3 (table 5).

Concentrations of major ions (Ca, Mg, HCO_3^-, and SO_4^{2-}) in water samples from all collection sites showed the effects of oxidation of sulfides. The increases in Ca and Mg, in conjunction with near-neutral pH values, suggest that acid production is being buffered by the dissolution of carbonates. Concentrations of heavy metals were low, possibly as a result of buffering. Slow dissolution reaction kinetics of primary minerals containing heavy metals, combined with a high rate of pore water flushing, could also have limited metal concentrations in discharge water.

The statistical significance of the differences between water quality at the upper and lower level sampling sites cannot be determined because of the small number of samples collected. However, water sampled on the upper level probably reflects the poorest quality recharge to the Barr stope, poorer than recharge from the surrounding bedrock, because this water comes from overlying sand-filled stopes. Also, water quality on the lower level reflects a more advanced degree of sulfide oxidation than does water at the upper level. This suggests that the water at B2 and B3 contains measurably higher concentrations of dissolved ions than water from all individual sources of recharge to the stope.

Saturation indices calculated using WATEQ4F [Ball, Nordstrom, and Zachmann, 1987 (*1*)] provide a basis for identifying the dissolution and precipitation reactions that may control the concentrations of elements in water samples (table 6). A saturation index greater than 0 indicates that a mineral will tend to precipitate, while a saturation index less than 0 indicates that a mineral will tend to dissolve. As suggested previously, the water at all sampling sites appears to be in equilibrium with carbonates.

Table 4.—Concentrations of elements above (B1) and below (B2, B3) Barr stope, milligrams per liter

Constituent	11/90	12/90		1/91		3/91		4/91		5/91		MCL
	B1	B1	B2	B1	B2	B1	B3	B1	B3	B1	B3	
Element:												
Al	0.37	0.60	0.67	<0.01	<0.01	0.61	0.55	0.21	0.19	0.27	0.30	NAp
As	<.10	.30	.20	<.10	<.10	<.10	<.10	NA	NA	NA	NA	[1]0.05
Ba	.02	.02	.02	.03	.01	.02	.02	.05	.02	.01	.03	[1]1.00
Ca	170.80	185.10	391.80	257.90	505.90	151.90	251.30	244.30	451.50	154.40	321.60	NAp
Cu	.07	.04	.03	.03	.03	.06	.06	<.01	<.01	<.01	.03	[2]1.00
Fe	.11	.06	.01	.47	.07	.66	.03	.31	.20	.49	1.23	[2].30
K	4.10	3.40	11.00	9.30	8.60	4.20	4.20	17.30	20.30	4.00	5.50	NAp
Mg	46.54	43.70	111.30	52.80	128.20	46.60	79.60	58.90	98.80	41.00	82.40	NAp
Mn	.79	.83	2.36	.89	2.11	.89	.04	1.06	.04	.73	.10	[2].05
Na	2.04	1.12	1.85	1.98	2.80	.22	.86	1.81	3.08	.89	1.57	NAp
Ni	<.01	<.01	.02	.02	.02	<.01	<.01	<.01	<.01	<.01	<.01	NAp
P	.11	<.05	<.05	<.05	.37	<.05	.16	.70	.58	.23	<.05	NAp
Pb	<.05	.16	.10	.07	.17	.21	<.05	<.05	<.05	<.05	.12	[1].05
Si	9.04	9.42	8.59	11.38	10.75	7.28	7.01	11.14	9.82	7.68	8.14	NAp
Zn	.08	.06	.35	.04	.34	.09	.13	.02	.12	.03	.12	[2]5.00
HCO_3	NA	NA	NA	250.00	319.00	250.00	305.00	256.00	315.00	264.00	305.00	NAp
SO_4	408.30	373.20	1,140.60	417.30	1,171.30	360.90	797.10	503.70	1,116.40	340.20	863.70	[2]250.00
pH	7.39	7.79	7.36	7.55	7.53	6.89	7.09	7.40	7.17	7.34	7.32	NAp
Eh	125.00	244.00	303.00	149.00	144.00	218.00	212.00	106.00	132.00	118.00	164.00	NAp
EC	.99	.97	1.76	.94	1.69	.93	1.55	.92	1.57	.94	1.48	NAp

EC Electrical conductance.
Eh Redox potential.
MCL Maximum concentration level.
NA Not analyzed.
NAp Not applicable.
[1]Primary standards.
[2]Secondary standards.

Table 5.—Concentrations of dissolved elements in water samples collected from sites B2 and B3 during May 1991, milligrams per liter

Constituent	B2	B3
Element:		
Al	0.24	0.30
Ba	0.01	0.03
Ca	303.60	321.60
Cu	<0.01	0.03
Fe	0.03	1.23
K	5.90	5.50
Mg	82.94	82.37
Mn	1.37	0.10
Na	1.49	1.57
Ni	<0.01	<0.01
P	0.56	<0.05
Pb	<0.05	0.12
Si	6.61	8.14
Zn	0.26	0.12
HCO_3^-	402.00	305.00
SO_4^{2-}	736.80	863.70
pH	7.35	7.32
Eh	146.00	164.00
EC S	1.66	1.48

EC Electrical conductance.
Eh Redox potential.

A list of minerals considered to be sources and/or sinks of the major ions detected in water samples from B1 and B3 were entered into BALANCE (table 7). For input to BALANCE, a saturation index between −1 and +1 is assumed to equal 0, indicating equilibrium conditions. BALANCE was used here to test whether a proposed set of dissolution and precipitation reactions could explain the water quality changes.

With the exceptions of dolomite [$CaMg(CO_3)_2$] and gypsum, minerals whose saturation index is 0 ±1 were considered to be both potential sources and potential sinks. Dolomite was considered only as a potential source because it does not precipitate readily under the conditions existing at the testsite. There is no gypsum in the mineralogy; therefore, gypsum was considered only as a potential sink. Illite occurs in significant quantities in the wall rock, but was not considered a potential source because its saturation index is much greater than 0.

Table 6.—Saturation indices for Barr stope water samples

Mineral	Sampling level	Sampling date					Average
		12/90	1/91	3/91	4/91	5/91	
Albite	Upper	−1.4	NC	−2.4	−1.4	−2.1	−1.8
	Lower	−1.3	NC	−2.0	−1.5	−1.8	−1.7
Calcite	Upper	.8	0.7	−.2	.5	.3	.4
	Lower	.6	.9	.2	.5	.5	.6
Ca-montmorillonite	Upper	5.6	NC	6.9	5.6	5.3	5.9
	Lower	6.4	NC	6.3	5.6	5.5	6.0
Dolomite	Upper	.7	.4	−1.1	.1	−.2	.0
	Lower	.5	1.0	−.3	.2	.3	.3
Ferrihydrite	Upper	1.7	1.7	1.1	.4	.6	1.1
	Lower	.9	.6	.1	−.1	1.6	.6
Gypsum	Upper	−.8	−.7	−.9	−.7	−.9	−.8
	Lower	−.3	−.2	−.5	−.3	−.4	−.4
Siderite	Upper	−2.4	−.4	−.8	−.7	−.4	−.9
	Lower	−3.3	−1.2	−2.0	−1.1	−.1	−1.5
Silica gel	Upper	−.4	−.3	−.5	−.4	−.5	−.4
	Lower	−.5	−.4	−.6	−.4	−.5	−.5

NC Not calculated.

Table 7.—Minerals examined during geochemical modeling

Mineral	Chemical formula	Source	Sink
Albite	$NaAlSi_3O_8$	X	
Ankerite	$CaFe(CO_3)_2$	X	
Calcite	$CaCO_3$	X	X
Dolomite	$CaMg(CO_3)_2$	X	
Ferrihydrite	$Fe(OH)_3$		X
Gypsum	$CaSO_4 \cdot 2H_2O$		X
K-feldspar	$KAlSi_3O_8$	X	
Montmorillonite	$(Al,Mg,Ca,Na,K)_8(Si_4O_{10})_4(OH)_8 \cdot 12H_2O$		X
Pyrite	FeS_2	X	
Siderite	$FeCO_3$	X	X
Silica	SiO_2	X	X

Two generalized models explaining the changes in observed water quality, with the constraints described above, were obtained using BALANCE (table 8). The dominant reactions of the first model included oxidation of pyrite by O_2, accompanied by dissolution of calcite and dolomite, precipitation of either ferrihydrite or siderite, and release of carbon dioxide (CO_2) gas. Dissolution of minor amounts of albite ($NaAlSi_3O_8$) and K-feldspar ($KAlSi_3O_8$), accompanied by precipitation of minor amounts of amorphous silica and montmorillonite, were also included in the first series of reactions.

The second model substituted dissolution of ankerite for calcite, while the other reactions remained the same. Inspection of an Eh-pH diagram (fig. 2) and the presence of deposits of yellow boy indicated that ferrihydrite was precipitating instead of siderite. On the basis of known mineralogy, the second model best represents existing conditions.

Table 8.—Mass transfer between backfill and infiltrating water calculated using BALANCE

Mineral	Change, mmol	
	Model 1	Model 2
Albite	+0.03	+0.03
Ankerite	NI	+2.47
Ca,K,Mg,Na-montmorillonite	-.02	-.02
Calcite	+2.47	NI
CO_2 gas[1]	-5.20	-7.68
CO_2 gas[2]	-2.49	-2.49
Dolomite	+1.70	+1.70
Ferrihydrite[1]	-2.72	-5.19
K-feldspar	+.04	+.04
O_2 gas[1]	+10.22	+12.07
O_2 gas[2]	+9.54	+10.78
Pyrite	+2.73	+2.73
Siderite[2]	-2.72	-5.19
SiO_2	-.13	-.13

NI Not included.
[1]Precipitation of ferrihydrite.
[2]Precipitation of siderite.

Note.—Plus (+) = dissolution; minus (-) = precipitation.

Geochemical models indicate that dissolution of carbonate minerals can explain the observed buffering of acid produced during pyrite oxidation. Concentrations of metals in water discharging from the Barr stope may be limited by this buffering action. WATEQ4F and BALANCE are thermodynamically based computer models that do not account for reaction kinetics.

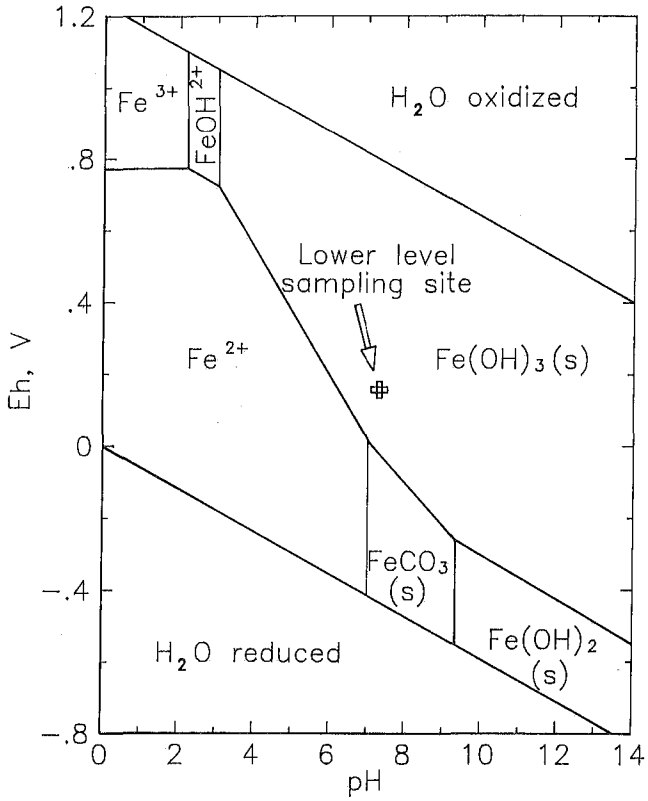

Figure 2.—Eh-pH diagram for ionic species and hydroxides of Fe in water from site B3 on 17 level. Ferrihydrite [$Fe(OH)_3$], siderite [$Fe(CO_3)$], and $Fe(OH)_2$ are solid phases.

DISCUSSION AND CONCLUSIONS

The most notable differences between assays of the 10-year-old and recently deposited sandfill samples were higher As, Cu, and Zn, and lower Mn in the new sandfill. These differences can be explained either by differences in ore grade or by the leaching of As, Cu, and Zn from the 10-year-old sandfill. The most notable differences observed from maximum leachability tests of the new and old sandfill samples were higher As, total S, and Zn, as well as lower Fe and Mn in the new sandfill. The higher S concentrations in the leachate from the new sandfill may have resulted from previous leaching of SO_4^{2-} from the old sandfill as a result of sulfide oxidation. The higher Fe and Mn concentrations in leachate from the old sandfill were probably derived from more soluble, oxidized secondary minerals in the old sandfill. Arsenic and zinc may have been leached previously from the old sandfill; however, differences in ore grade is a more probable explanation.

Concentrations of major ions (Ca, Mg, HCO_3^-, SO_4^{2-}) in water samples from all sampling sites show the effects of sulfide oxidation. The increases in SO_4^{2-}, Ca, and Mg, in conjunction with near-neutral pH values (table 4), suggest that acid production may be buffered by dissolution of carbonates.

The dominant reactions determined using the computer models WATEQ4F and BALANCE included oxidation of pyrite by O_2 accompanied by dissolution of ankerite and dolomite, precipitation of ferrihydrite, and release of CO_2. Thus, dissolution of carbonate minerals can explain the observed buffering of acid produced during pyrite oxidation. The concentrations of metals in water discharging from the Barr stope may be limited by this buffering. Alternatively, slow dissolution reaction kinetics of primary minerals containing metals may limit concentrations.

The average concentrations of dissolved constituents detected in water from above and below the Barr stope were much lower than the concentrations detected in the worst acid-producing areas of the mine. During one or more sample visits, concentrations of many constituents in water from the three sampling sites exceeded the concentrations in mine recharge water as well as the MCL's set forth in the Safe Drinking Water Act. However, only SO_4^{2-} consistently exceeded the MCL's. Also, water from the lower level had higher concentrations of many of the products of sulfide oxidation than did water from the upper level.

Extrapolating the results of this study to the future when the sandfilled stope is flooded requires an understanding of changes in the controlling geochemical reactions and the rate of ground water flow through the sandfill. Once the sandfill is flooded, the rate of oxidation of sulfide minerals will be much lower, resulting in less acid being produced and therefore less associated mineral dissolution. Metals contained in secondary minerals in oxidized backfill may be released after the backfill is submerged. However, if significant amounts of metals were contained in secondary minerals in the sandfill, they would have been leached along with Fe and Mn during the acid leachability test.

The degree to which the sandfilled stopes constitute preferential ground water flow pathways depends on their degree of interconnection and their hydraulic conductivity relative to the surrounding bedrock (the natural aquifer). In the case of the Barr stope, the hydraulic conductivity of the sandfill is expected to be approximately two orders of magnitude greater than that of the bedrock. Also, the Barr stope is connected to an extensive system of sandfilled stopes. Ground water flow will be channeled preferentially through the sandfilled stopes when the ground water flow system reaches a new equilibrium. Nonetheless, flushing of the sandfill by ground water will be much less after the stope is flooded because the mine will no longer act as a drain.

To summarize, the most important result of this research is that concentrations of metals in water discharging from the Barr stope remained below or only slightly above MCL's. Buffering of acid by dissolution of carbonate minerals may account for the lack of metals release from the sandfill. Metals release after mine flooding is expected to remain low because of the buffering capacity of the sandfill and a reduction in the rate of oxidation.

Some metals release from secondary minerals in the sandfill may occur, but at a rate that should be no greater than that observed during this study. The sandfilled stopes in the mine will probably act as preferential ground water flow paths after the mine is flooded, but the flow rate will be greatly reduced. The overall impact of this specific sandfilled stope is expected to be small because of the combination of decreased sulfide oxidation, the apparent lack of metals contained in secondary minerals in the sandfill, and decreased metals transport resulting from lower ground water flow rates.

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